

Application Date	5 <sup>th</sup> Jun., 1987
Series No.	87109044
Class	D26M10/00

Description of the Invented/Other Application Patent		
I. Name of Invention/New Application	Chinese	
	English	Fibrous Products Surface Treatment / Modification Method
II. Inventor / Creator	Name	1. Zheng ShuHui; 2. Liao JunDe; 3. Liu YouTai; 4. Hu YanRong
	Nationality	Taiwan, China
	Address	1. No. 321, section 2, GuangFu Road, Hsinchu city 2. No. 155, section 1, people Longli Taichung port road, West Taizhong
III. Applicant	Correspondence Name	1. Group Legal Representative Industrial and Technology Institution 2. Liao JunDe
	Nationality	Taiwan, China
	Correspondence Address	1. No. 195, section 4, zhongxing road, Chudong, Hsinchu province 2. No. 155, section 1, people Longli Taichung port road, West Taizhong
	Representative Name	1. Sun Zheng

Revised on 6th Dec.,

IV. Abstract - Chinese (Invention Name: A method of Surface Treatment and Modification on Fibrous products and making the same )
<p>Abstract – English (Invention Name: A method of Surface Treatment and Modification on Fibrous products and making the same )</p> <p>This invention includes a surface treatment method applicable to various fibrous products. The process was done in a high ion density microwave plasma system. Fibers are first activated to form free radical on surface, then grafted with functional monomers. The modified fiber products possess many advantages such as diversities, easy processing and permanence. Those functionalized textile products can be applied to battery separator, biomedical materials and etc.</p>

#### V. Description (1)

##### **Technical Field**

This invention is about a surface treatment method applicable to various fibrous products. It is done by first using the microwave plasma to activate the fibers' surface, then grafting the functional monomers onto the fiber surface to gain the specific function.

##### **Background**

The synthetic fibrous products have been widely used on biomedical uses and electronic products, such as surgery tools, biomedical material, sanitary products, blood segregator, battery separator etc., in recent years. It is not only because of its feature as quick production circle but also because of its stabilization, isolation and permeability etc. The material required to make these products needs to hold special characteristics such as water affinity, water sparse, infiltration capacity or functional surface etc. Thus the fibre needs to have the surface modification treatment first to enhance the properties. Generally speaking, the surface modification techniques could be divided two methods known as the chemical and the low pressure treatment. The chemical treatment is done by sink the material into the chemistry. By soaking the chemistry, the material can gain certain features. But one disadvantage of this method is it often has the problem of surface chemistry falling off, which not only reduces the service life of the material but also creates the environmental pollution by producing large amount of harmful waste water. As for low pressure treatment, the mostly potential way is to use low temperature, high ion density microwave plasma to process the material in order to extend active time of the surface free radical or create stable decomposable preoxide. Microwave plasma assist chemical treatment could grafting functional monomers onto the fibre surface. It is the needs from the industry in terms of environmental protection.

Basically, textile fiber surface intensifies after being physics, and temporary free radical will be formed in the near surface. This could be used to develop certain specific feature into the material by grafting its monomers. Normal electric plasma caused by discharging the electricity pole plate. It has the problem, as treated for a while, as losing the free radical once the material being heating. It would be hard to grafting the functional monomers to modified it. Besides, the strength of the textile might also be changed.

-3-

## V. Description (2)

There are more than 10 kinds of above normal temperature, high temperature or low temperature plasma in the world in modifying the fiber surface feature. Different effects showed as the difference among the electric wave equipment and material. As presented in the US Patent US9368508, it could enable the non-woven cloth to have the wet ability by using plasma under normal temperature. The disadvantage of this method is that it needs longer process time due to low energy ion density under normal temperature. Thus it could easily damage the textile fiber surface by creating high/hot temperature on the surface, reduce the mechanical strength of the material, and difficulty in grafting monomers with textile fiber

Presented in the Japanese patent JP05295662 is a method of using plasma for grafting monomers to process the polyester fabric under low temperature high Radio Wave (Radio Frequency,  $\leq 13.56\text{MHz}$ ). The shortcoming of this method is the density of plasma has its limit which could only process limited area on the textile fabric. Besides, it also has the design difficulty in balancing the uniformity of the plasma. Further, the method of process the material in between electricity pole plates to increase the plasma density will break the fibre surface and the grafting uniformity due to the increased treatment period.

The method including in this invention, the surface treatment and modification on Fibrous Products, is to use low temperature microwave plasma for grafting monomers in order to improve/solve the above problems. It has the advantage of simple production, quick, stabilization, uniformity according to the grafting density and process time. Because it could be used for treating large amount of products, it is practical to use this method in the commercial production

## Briefing of the Invention

The invention, the surface treatment and modification on Fibrous Products, is created

based on the concept of first forming free radicals by using low temperature microwave plasma to activate the fibers' surface. Then by grafting monomers it enable the sample to have the feature of water affinity or the sparse water and so on. It could improve the sustainability of the fiber's active surface due to the reduced treatment time. It also did little changes to the fiber strength itself. Furthermore, the treatment has the advantages of easy process and permanence. The water affinity treated material could be used for battery separator or biomedical material due to the good quality

-4-

## V. Description (3)

### Simple Chart Illustration

Chart I is the flow chart of the processing method

Chart II is the illustration of the device, the respective figures represent the following parts, 1. Energy Source 2. Energy Producer 3. Energy Controller 4. Cooling Water 5. Gas Mixing Room 6. Belt Drive Wheel 7. Metal Pipe 8. Vacuum Pump 9. Rolling Machine 10. Microwave Plasma Activating Room 11. Microwave Plasma Grafting Room 12. Samples 13. Temperature Controller 14. Gas

Chart III is to show the relationship between water soakage and time while grafting acrylic acid onto non-weave polypropylene cloth while adopting the method

### Detail Illustration of the Invention

The flow of the treatment for this invention, the surface treatment and modification on Fibrous Products, is as illustrated in Chart I. Pre-treat the textile fiber product, then pass through activate gas, grafting monomers and finally has the pro-treatment to achieve special functional fibrous products.

The main characteristic of the invention lies in: using low temperature in activating and grafting; the microwave frequency is more than 1GHz, which performs better in the range of 1.5-3GHz, and the normal range is around 2.45 GHz (according to the generator). The high density microwave plasma will not only be harmless to the surface of the fiber, but also release free radical evenly on the textile fiber surface and enable the material with water affinity or water sparse by grafting with functional monomers.

-5-

## V. Description (4)

Fiber as Polyethene or polyester could be produced into special functional fibrous products due to its no polar group molecular structure which allow itself to be waterproof. By treated with the microwave plasma from this invention, the fiber could form free radicals after the, C-C, C-H ect., key place stopped chains which could be used to adjusted into different monomers mixture density to further control the grafting density to produce special functional Fibrous products.

The gas involved in this invention includes the inert gas, such as He, Ar and so on, and non- inert gas, such as O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, S<sub>2</sub>, SO<sub>2</sub>, F<sub>2</sub> and so on. These gases could form the high energy gas molecules, ions and free radicals under certain control. The different combination and category of the gas could affect the type of monomers, way of grafting strength of the grafting when functional monomers tie to the fiber. The methods hold different treatment result as to different material, process. So as to the functions the material received.

Certain temperature needs to be controled to influence the monomers for grafting in this

invention. The monomers will only start to react under certain degree, which vary from different material. The temperature should be controlled under the material Softening Temperature.

The monomers used in this invention includes but is not restricted in the acylic acid,2-hydroxyethyl methacrylate, hydroxypropyl methacrylate or methacrylic acid

The textile fibre mentioned in this invention includes non-woven cloth and fibric. The raw material of these fibrous products includes but is not restricted in the polyethylene, polypropylene, polyamide, polyester or armatic polymer

The polar-polar interaction bewteen polar surface of the fiber and water hydrogen bond is the main reason that the ability of water affinity could be increased after the treatment with plasma

The invention will be further discussed by the following cases. But the cases only serve for illustration instead of contrain the scope of the invention

-6-

## V. Description (5)

### 5. Cases

#### Case 1

Use the device illustrated in Chart II, and use rolls of PP non-woven cloth as the test specimen(12). Before start, pull out the vacuum from the plasma equipment by vacuum pump to 0.2mbar. The highest output of the microwave plasma machines in this invention is 2Kw, with operation pressure 0.2mbar, frequency 2.45GHz. The main process could be divided into four parts, first the test specimen (12) goes through a pre-treatment process as using gas Ar (14a) to purify the material surface. Then go to active room(10), energy controller (1,2,3) in turn. Wattz needs to be adjusted here to control the plasma. After activated, the test specimen enters into a grafting room (13) with 80°C temperature control(13). The acrylic acid monomer (14c) will be grafted to the sample surface. When it's done, the sample will be taken into the post-processing treatment. Ar (14d) is being used here to blow the residual monomer, roll out agin to takes shape (9). The textile fiber product would have the extremely good water affinity after the whole process.

Non-woven cloth could have lower liquid interface, even gain some wettability after the gas activation. It could be teached to have stablized water affiniity and hygroscopticity characters after grafting monomers.

#### **Comparison Case I**

Compare the difference between the water affinity ability gained under high electic wave plasma and this method while activated under same condition. EVAluate methods in terms of JIS-LI096. It could be found that although the interface could be improved for the non-woven cloth under the high electric wave plasma, the weave's mechanical strength can't be reduced. On the contrary, the treatment under this invention showed extremly superior water affinity.

-7-

## V. Description (6)

Micro-wave Plasma

Time

0 sec.  
10 sec  
15 sec  
30 sec  
60 sec  
90 sec

Wet-abilities

Dry  
Part Wet  
Part Wet  
Completely Wet  
Completely Wet  
Completely Wet

Strength

3.52  
kg/50mm  
3.52  
kg/50mm  
3.52  
kg/50mm  
3.52  
kg/50mm  
3.52  
kg/50mm  
3.52  
kg/50mm

High Electric Wave Plasma

Time  
0 sec.  
10 sec  
15 sec  
30 sec  
60 sec  
90 sec

Wet-abilities

Dry  
Dry  
Lower Interface with the surface dry  
Lower Interface with the surface dry  
Lower Interface with the surface dry  
Lower Interface with the surface dry

Strength

3.52

3.22

3.44

3.21

3.22

3.02

## Case 2

Use the dynamic interface meter to analyze the test specimen's water absorption volume, as compared with time, under the activation and grafting process of this invention. As shows in Chart III, test specimen weight 10mg with the initial absorption speed of 80mg/sec., average 1.92mg/sec. And the absorption speed has been increased to 210mg/sec right after using the acrylic acid for grafting, average 3.8mg/sec.

## 6. Function

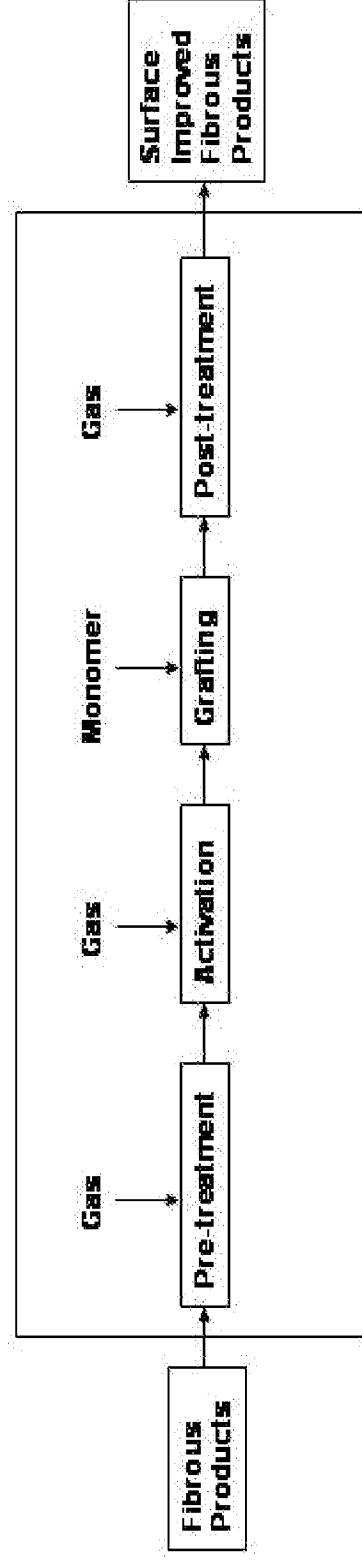
The surface treatment/modification method for fibrous products invented here, could, by using high density low temperature plasma, form free radical evenly onto the fibre surface thus to graft functional monomers. It solves the problems as too low density for grafting and the fibre surface destructed while using high radio wave plasma (-13.56MHz). Instead, the fiber could maintain relatively high strength and special features such as water affinity or water sparse. Besides, it could treat big area each times. It is a high productivity and environmental protection surface treatment.

-8-

## VI. Applied Range of Patent (Claims)

1. A surface treatment to fibrous products, also called surface improvement/modification method, includes first activating the fibers' surface by using high ion density microwave plasma to form free radical onto surface, then grafted with functional monomers to gain specific water affinity function
2. The micro wave plasma according to claim 1 wherein it could produce high ion density microwave plasma
3. The frequency of micro wave plasma according to claim 1 should be more than 1GHz.
4. The frequency of micro wave plasma according to claim 3 whereas the better frequency should be within 1.5-3GHz
5. The frequency of micro wave plasma according to claim 4 whereas the best frequency should be 2.45GHz.
6. The gas to activate the fibre surface according to claim 1 is the mixture of O<sub>2</sub>, He, Ar
7. The monomers according to claim 1 is consisted of acrylic acid, 2-hydroxypropyl methacrylate and methacrylic acid
8. The fibrous products according to claim 1 includes non-weave cloth and fabric
9. The raw material used for the fibrous products according to claim 1 is combined with polyethylene, polyamide, polyester and aromatic polymer

-9-



**Microwave Plasma  
Surface Treatment**

**Chart I**

